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(54) Abrasive hard surface cleaning compositions

(57) The invention provides aqueous acidic cleaning compositions with a paste-like consistency comprising an abrasive, an acid, an anionic surfactant able to form a structured liquid with dilute acid, and an acid-stable thickener. The compositions are excellently suitable for cleaning a large variety of soils and stains including lime scale and rust stains by a combination of mechanical (abrasive) action and chemical action/dissolution.

EP 1 460 125 A1

Description

TECHNICAL FIELD

[0001] The present invention relates to cleaning compositions for hard surfaces comprising an abrasive. More particularly the invention relates to hard surface cleaning compositions which are effective in removing lime scale and rust.

BACKGROUND AND PRIOR ART

[0002] Abrasive hard surface cleaning compositions are well known in the art. Whereas many years ago such compositions were only available as powders, in the last decade liquid compositions have grown much more popular. Such compositions are easily dispensable creamy liquids and are more attractive to the consumer from a sensory and visual point of view. However, they are generally more expensive than powders.

[0003] Most of these compositions have alkaline pH and are therefore very effective for removing most stains and fatty soils. However, for removing lime scale and rust stains on toilet and bathroom surfaces they are only moderately effective. To this end acidic compositions have been developed which tend to be more effective in removing lime scale and rust stains. These compositions may contain one or more of a variety of organic and/or inorganic acids. Particularly for rust removal oxalic acid is often included.

[0004] Thus, US 5,460,742 describes acidic cleaning compositions. They are thixotropic liquids comprising 5-50% abrasive, amphoteric and nonionic surfactant and a hydrated aluminium silicate thickener (thickening clay).

US 3,579,456 describes pourable acidic liquid cleaners comprising up to 60% abrasive, up to 10% polyvalent organic acid, anionic detergent and ammonio-zwitterionic detergent.

US 4,561,993 discloses thixotropic liquid abrasive cleaners, comprising up to 20% mineral acid, up to 2.5% surfactant, not being anionic surfactant, up to 12% precipitated silica suspending agent and up to 15% abrasive.

JP-A-53139606 describes acidic cleaners being viscous liquids comprising a mineral or organic acid and a thickening clay. They may additionally contain an abrasive.

[0005] Many other acidic rust removing compositions are known in the art. Some are powders and may contain an abrasive component; others are liquids which may or may not be thickened to increase the viscosity, but which do not contain abrasive and thus remove rust or lime scale only by dissolving it.

[0006] There is a need for a rust and lime scale removing product which has the advantages of a liquid abrasive cleaner as to ease of dispensing and sensory and visual appearance, but which is more economical in use and after being applied to a stain, particularly on an inclined or vertical surface, can remain in prolonged contact with that stain, thus providing chemical removal or dissolution of the stain.

BRIEF DESCRIPTION OF THE INVENTION

[0007] It has now been found that aqueous acidic abrasive hard surface cleaning compositions may be prepared in the form of a paste which are excellently suitable for cleaning a large variety of soils and stains including lime scale and rust stains by a combination of mechanical (abrasive) action and chemical action/dissolution. Such pastes are easy to apply in the required amount and are thus economical in use.

[0008] Thus, the invention provides aqueous acidic cleaning compositions with a paste-like consistency comprising an abrasive, an acid, an anionic surfactant able to form a structured liquid with dilute acid, and an acid-stable thickener.

[0009] Furthermore, the invention provides a process for removing rust or lime scale stains from a hard surface comprising the step of applying the paste to the stain.

DETAILED DESCRIPTION OF THE INVENTION

[0010] All percentages mentioned herein are "by weight", unless specifically mentioned otherwise.

[0011] As mentioned above, the acidic cleaning compositions according to the invention are pastes. Thus, they are very viscous, sluggish flowing liquids. Pastes can be characterised by having a low shear stress (<10Pa) plateau viscosity value of >1000 Pa.s, and producing pronounced shear thinning at a shear stress of about 1000 Pa and above.

[0012] The pastes according to the invention are acidic and have a pH between 0 and 3, preferably at or below 2.5, more preferably at or below 2 or even 1. Thus, they contain a mineral and/or organic acid in the required amount to give the desired pH, generally in an amount of 5-25% calculated on the liquid phase (which for the purposes of this invention is defined as the total composition minus the abrasive). Preferably they contain at least a mineral acid and suitable examples thereof are hydrochloric, sulphuric, sulphamic and phosphoric acid, preferably in an amount of 5% of the liquid phase or more. Sulphuric and sulphamic acid are particularly preferred. The compositions may additionally contain up to 15% of the liquid phase of an organic acid, particularly a di- or poly-carboxylic acid. Oxalic and citric acid are suitable examples.

[0013] The pastes according to the invention comprise a solid particulate abrasive in amounts of between 20 and 75% of the total composition, preferably 30-65%, more preferably at least 40%. Suitable abrasives have Mohs hardness of 7 or below, but preferably above 1. Preferably the hardness is at least 2.

[0014] Suitable abrasives are stable in the acidic en-

vironment of the compositions according to the invention and can be selected from inorganic abrasives such as silicas, silicates, aluminosilicates, aluminas, perlite, pumice and gypsum; organic polymeric abrasives such as polyethylene, polycarbonate, polyurethane, polystyrene, polypropylene, polyethylene terephthalate, polymethylmethacrylate and nylon; and natural abrasives such as ground nutshells; and mixtures thereof. A special class of abrasives is formed by inorganic salts which are sparingly soluble in water and are used in an amount above their saturation solubility. Suitable salts in this category are Na tripolyphosphate, Na tetraborate and K sulphate.

Preferred abrasives are: aluminosilicates, alumina, hydrated alumina, feldspar and silica. Especially preferred are feldspar and silica, and combinations of any of those with gypsum in which feldspar and/or silica make out at least 25% of the abrasives mixture.

[0015] Suitable weight average particle sizes for the abrasives fall in the range 0.5-500μm. In this range an acceptable compromise between good cleaning behaviour and low substrate damage can be achieved. Weight average particle size values of 5-100μm are preferred and 10-50μm particularly preferred.

[0016] Furthermore, the pastes according to the invention comprise an anionic surfactant which is suitable to form a structured liquid with the acidic aqueous phase. The structured liquid is able to provide a stable suspension of the abrasive in the liquid.

[0017] A suitable class of anionic surfactants are organic sulphuric acid mono-esters and sulphonic acids having in the molecular structure a branched or straight chain alkyl group containing 8-22 C atoms or an alkylaryl group containing 6-20 C atoms in the alkyl part. Particularly suitable are sulphonates, more particularly:

- alkylbenzene-sulphonates, such as those in which the alkyl group contains from 6 to 20 carbon atoms and is preferably straight-chain;
- alkanesulphonates, preferably secondary alkanesulphonates, more preferably those having 10-18 C atoms in the alkyl chain.

The anionic surfactant is preferably used in an amount of 2-25%, more preferably 6-20% of the liquid phase.

[0018] To further obtain the required paste viscosity the compositions according to the invention preferably comprise a sufficient amount of an acid-stable thickening agent. Thickening silica and thickening clays well known in the art are very suitable for this purpose. Suitable thickening clays belong to the group of smectite clay minerals specifically the bentonite- or montmorillonite-type clays. They are preferably used in an amount of 2-25%, more preferably 5-15% of the liquid phase. Compositions with a low level of abrasive preferably contain enough thickening silica or clay to give a total level of insoluble solids of at least 35% of the total composition.

[0019] The compositions according to the invention may comprise other components known in the art as being suitably added to cleaning compositions. Thus they may contain additional surfactants, particularly nonionic or amphoteric surfactants known in the art, provided that these do not interfere with the liquid structuring properties of the anionic surfactant or surfactants present. Suitable surfactants are described in the well-known textbooks: "Surface Active Agents" Vol.1, by Schwartz & Perry, Interscience 1949; "Surface Active Agents" Vol.2 by Schwartz, Perry & Berch, Interscience 1958; the current edition of "McCutcheon's Emulsifiers and Detergents" published by Manufacturing Confectioners Company; "Tenside-Taschenbuch", H. Stache, 2nd Edn., Carl Hauser Verlag, 1981. However, in general addition of nonionic and/or amphoteric surfactants does not provide substantial additional benefit to the compositions according to the invention, but does add to the cost. Therefore preferably at most either a nonionic or an amphoteric surfactant is present and most preferably neither of these.

[0020] Generally, the presence of zwitterionic or cationic surfactants does not serve any useful purpose at all and compositions without such surfactants are a preferred embodiment of the invention.

[0021] The compositions according to the invention may contain organic solvents to aid in the cleaning properties of the compositions. Suitable solvents are e.g. C1-C4 aliphatic alcohols and mono- or di- ethylene or propylene glycols or mono-ethers thereof with C1-C6 aliphatic alcohols.

[0022] Further additional components that may be present include: perfumes, dyes, optical brighteners, antimicrobials/bactericides, halogen or peroxide bleaching agents, etc.

[0023] The compositions according to the invention are preferably packed in containers such as a tub or tin, from which suitable amounts can be taken out on a suitable applicator such as a wet cloth or sponge, or in containers from which they can be dispensed by squeezing, such as a tube. Containers from which they can only be dispensed by pouring are less suitable in view of the sluggish flow characteristics of the compositions. The compositions according to the invention provide excellent cleaning on a large variety of soils and stains, but particularly on soils and stains prevalent on bathroom and toilet surfaces, such as soap scum, lime scale and rust. They are more versatile in use and easier to dose than powdered products. They give more concentrated cleaning on tough soils than liquid abrasive cleaners and an overdose of the product can easily be removed and used again by putting it back in the tub or tin packaging. Also, when applied to rust or lime scale stains and left to dissolve these, they give improved cleaning because of better cling, and therefore prolonged contact time, than liquid abrasive cleaners.

[0024] Thus, the invention also provides a process for removing rust and lime scale stains from hard surfaces,

comprising the steps of applying a composition according to the invention to the stain, leaving the composition on the stain for a sufficiently long time to remove all or part of the stain by dissolution, if desired remove the remainder of the stain by mechanical abrasive action, and removing the composition by wiping and/or rinsing.

[0025] The compositions according to the invention can be prepared according to methods known in the art i.e. by mixing the ingredients in any suitable order. If a thickening silica or clay is used these are preferably first added to the mixture of acid and water and given sufficient time to hydrate before the abrasive is added under stirring. The anionic surfactant is preferably added as the last component. The paste structure develops after the anionic surfactant is added and may take between one and three days to fully develop.

Example

[0026] An acidic abrasive cleaning paste was prepared with the composition mentioned below (all percentages based on the total composition)

Abrasive: Feldspar FK45	60%
Thickening clay: MPV200 clay	3%
Anionic surfactant: LAS Isorchem 113	4%
Sulphuric acid	2.5%
Perfume	0.2%
Water	to 100%

Claims

1. Aqueous acidic cleaning compositions comprising and acid and an abrasive **characterized in that** they have a paste-like consistency and comprise an anionic surfactant able to form a structured liquid with dilute acid, and optionally an acid-stable thickener.

2. Compositions according to claim 1 **characterized in that** the pH of the composition is between 0 and 3

3. Compositions according to claims 1 or 2 **characterized in that** they comprise a mineral acid.

4. Compositions according to claim 3 **characterized in that** the mineral acid is chosen from sulphuric acid and sulphamic acid.

5. Compositions according to claims 1-4 **characterized in that** they additionally comprise a di- or polycarboxylic acid.

6. Compositions according to claims 1-5 **characterized in that** they contain 20-70% of a mineral abrasive with Moh hardness of between 1 and 7 and a weight average particle size between 0.5 and 500μm.

7. Compositions according to claims 1-6 **characterized in that** the anionic surfactant is chosen from alkyl-benzene sulphonates and secondary alkane sulphonates and is present in an amount of between 2 and 25% of the liquid phase.

8. Compositions according to claims 1-7 **characterized in that** the acid-stable thickener is chosen from thickening silica and thickening clay and is used in an amount of 2-25% of the liquid phase.

9. Process for removing rust and lime scale stains from hard surfaces, comprising the steps of applying a composition according to the invention to the stain, leaving the composition on the stain for a sufficiently long time to remove all or part of the stain by dissolution, if desired remove the remainder of the stain by mechanical abrasive action, and removing the composition by wiping and/or rinsing

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EUROPEAN SEARCH REPORT

Application Number
EP 03 25 1668

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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
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X : particularly relevant if taken alone
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